HETEROGENEOUS STRUCTURE AND IRREVERSIBLE ENTHALPY RELAXATION IN LIQUID DIBUTYLPHTHALATE(Session III : Complex Fluids, The 1st Tohwa University International Meeting on Statistical Physics Theories, Experiments and Computer Simulations)

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In liquids and glasses, some short-range structural order to be named a structured cluster may exist among the molecules, and the cluster size increases with decreasing temperature. The relaxation time, τ, for equilibration process becomes long gradually with the decrease. Three characters have been mentioned concerning the relaxations; non-Arrhenius property of the average relaxation times, nonexponentiality of the relaxation function, and nonlinearity of the function. The degree of non-Arrhenius property has been defined, according to a "strong-fragile" concept by Angell, by fragility m;

$$m \equiv \left. \frac{\mathrm{d}\log\tau(T)}{\mathrm{d}(T_\mathrm{g}/T)} \right|_{T=T_\mathrm{g}}, \qquad (1)$$

where T_g is the glass transition temperature. The nonexponentiality has been often discussed by using a parameter, β, in the stretched exponential function (namely KWW equation);

$$\Delta H_\mathrm{c}(t) = \Delta H_\mathrm{c}(0) \cdot \exp\left\{-(t/\tau)^\beta\right\}, \qquad (2)$$

where $\Delta H_\mathrm{c}(t)(= H_\mathrm{c}(t) - H_\mathrm{c}(\infty))$ denotes configulational enthalpy which should relax. We have defined nonlinearity parameter, δ, by the following expression;

$$\delta \equiv \frac{\mathrm{d}(\beta/\beta_0)}{\mathrm{d}(\Delta_\mathrm{j}T/T_\mathrm{a})}, \qquad (3)$$

where β_0 is the β value at $\Delta_\mathrm{j}T = 0$ K.

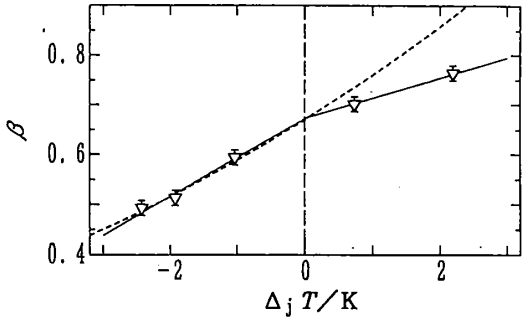

Fig. 1 Dependences of β on $\Delta_\mathrm{j}T$.

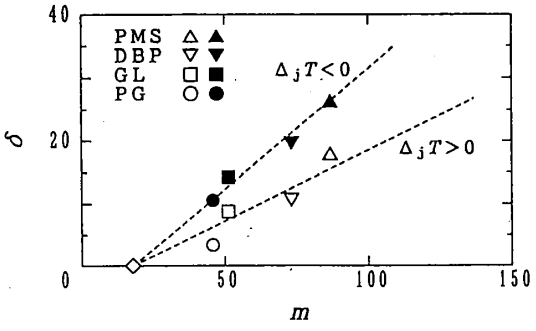

Fig. 2 Correlation between δ and m.

The enthalpy relaxation processes of dibutylphthalate (DBP, $m = 73$) under constant temperature condition were studied by the temperature jump method [1]: The temperature of sample in equilibrium at T_i was changed suddenly to T_a and the enthalpy relaxation was tracked at the constant temperature T_a. The experimental results were characterized by eq.(2) and the obtained β was plotted as a function of the temperature jump, $\Delta_\mathrm{j}T = (T_\mathrm{a} - T_\mathrm{i})$, in Fig. 1. Figure 2 shows the derived δ value as a function of m. A diamond represents the value for the "strongest" liquid which is expected to show a linearity in the response to temperature jump. Dotted lines are guides for eyes. It is deduced that a reasonable linear relation holds between δ and m for each of the positive and negative $\Delta_\mathrm{j}T$.

The thermal activation model for relaxation process is adapted to the DBP like system [1].

When the potential barrier for the molecular rearrangement is independent of temperature, the relaxation times should obey Arrhenius equation. The non-Arrhenius property of the average relaxation times, on the other hand, indicates that the activation energy changes along with temperature because of distribution of activation energy due to presence of clusters. The distribution of activation energy was reflected by the β_0 value, and the activation energy increased with decreasing temperature according to the fragility, m. The obtained $\Delta_j T$ dependence of β is shown in Fig. 1 with a thick dashed line. The agreement between the β values by the simulation and experiment is complete quantitatively on the negative side in $\Delta_j T$. This indicates that the present model reproduces well the structural relaxations in the exothermic, namely cluster-developing, processes On the positive side in $\Delta_j T$, on the other hand, the deviation of the β values by the simulation from the experimental results is large, indicating that the real processes are different from those pictured from the model or involve another factor.

Tool-Narayanaswamy model (TN model), applied to the analyses of DSC curves introduces the nonlinearity parameter, x, through the expression for $\tau(T, T_f)$;

$$\tau(T, T_f) = A \exp\left[\frac{x\Delta H^*}{RT} + \frac{(1-x)\Delta H^*}{RT_f}\right], \tag{4}$$

where A is a constant, ΔH^* is the apparent activation energy, R is a gas constant, and T_f is the fictive temperature supposed to represent the structure of liquid. The model supposes first that the β value in eq. (3) is a constant inherent to each substance at least within a small temperature region, second that the relaxation time, $\tau(T, T_f)$, is expressed by using T_f as characterizing the whole liquid structure at each moment, and thirdly that the nonlinearity of the relaxation functions is characterized by a constant value, x. The distribution of activation energies, according to the above simulation, changes severely during the relaxation as shown in Fig. 3. Thus the β would not be constant as a function of $\Delta_j T$, and the structure represented by T_f halfway through the relaxation is quite different from that at $T = T_f$ at equilibrium. After all, considering that the liquid has a microscopically heterogeneous structure, the TN model would contain some inadequacy in making a real physical picture for the structural relaxation in liquid.

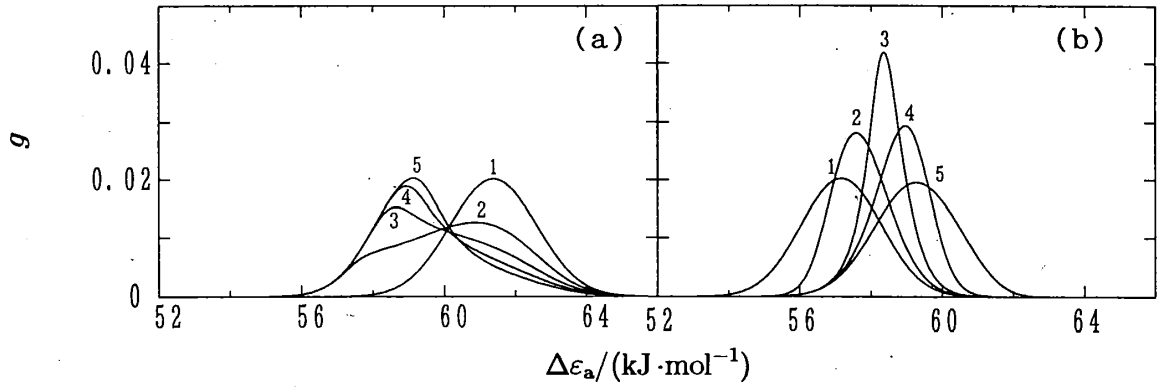

Fig. 3. Time evolution of the distribution of activation energies during the relaxation. (a) after the jump from 170 K to 172 K, (b) after the jump from 174 K to 172 K.

[1] M.Mizukami, H. Fujimori and M. Oguni, *J.Phys.:Condens. Matter*, **7**, 6747 (1995)